Comparative Measurement of Interfacial Tension by Transient Dynamic Methods

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ABSTRACT: An experimental comparison between different techniques for the interfacial tension measurement is presented for polyamide-6 and polystyrene pair. The techniques are transient dynamic methods, which include the breaking thread (BT) method, the imbedded fiber retraction (IFR) method, the deformed drop retraction (DDR) method, and two modified DDR methods. The modified DDR methods combine the analytical power of the DDR method with experimental simplicity of the BT and IFR methods, respectively. Interfacial tension values obtained by the modified DDR method that combines the BT method is much lower than those by the other methods. Among all techniques, the modified DDR that combines the IFR method is found to be most convenient and accurate method. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1910–1918, 2006

Key words: interfacial tension; breaking thread; imbedded fiber retraction; deformed drop retraction; transient dynamic method

INTRODUCTION

Interfacial tension between immiscible polymers is a critical factor for the morphology and final properties of the blend.[1,2] The increasing researches on polymer blend have lead to demand for methods to measure the interfacial tension between polymer pairs with greater accuracy and convenience. Several methods for the interfacial tension measurement have been developed but only a few methods are suitable for high-viscosity polymer melt.[3] The methods that have been tried for polymer melts are divided into equilibrium methods and transient dynamic methods. The former is adoption of the methods used for low-viscosity liquids. These methods include the pendant drop method,[4–6] the sessile drop method,[7] and the spinning drop method.[8,9] These methods require an accurate measurement of the steady-state shape of the liquid–liquid interface and the density difference. Because most polymer pairs have high viscosities, low interfacial tension values, and low density differences, the time to an equilibrium is very long, which leads to the thermal degradation of polymer melts and inaccurate interfacial tension value.

On the other hand, the transient dynamic methods can overcome this difficulty. In these methods, the interfacial tension is obtained by observing the shape evolution of the interface. Several methods, such as the breaking thread (BT),[10–13] imbedded fiber retraction (IFR),[14–17] and deformed drop retraction (DDR)[18] method, have been developed.

The BT method is based on the well-known experiments and analysis by Rayleigh[19] and Tomotika[20] on viscous liquids. When a droplet is highly extended under a certain flow field or a long polymer thread is surrounded by a matrix of another polymer, the capillary instability results in sinusoidal distortions on the interface. The distortion grows with time and ultimately the thread disintegrates into small droplets. To avoid end pinching, fiber retraction, and irregular distortion growth (which produce experimental errors), the length to diameter ratio of the thread must be very high and the diameter must be spatially uniform. Additionally, the system should have viscosity ration less than unity to get a regular sinusoidal distortion. Practically, these requirements are not easy to attain.

The IFR method was first introduced by Carriere et al.[14–16] In this method, the interfacial tension is evaluated from the shape change of a short fiber of one polymer imbedded in another polymer. This method overcomes the experimental difficulties encountered in the BT method. However, because the mathematical model in the IFR method is not purely analytical but semiempirical, empirical parameters should be determined by best fitting the experimental data to a system of known interfacial tension. Cohen and Carriere[15] determined the empirical parameter with PS/PMMA, a system of known interfacial tension. They estimated interfacial tension value of PS/PMMA, for

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determining the empirical parameter, by extrapolating the data of Wu.[21] Since then, all studies using the IFR method measure the interfacial tension using the empirical parameter determined by Cohen and Carriere, without any verification.

Most recently, Luciani et al.[18] and Guido and Villone[22] proposed a new method, which can overcome the limitations encountered in the BT and IFR method. In the DDR method, interfacial tension is obtained by the shape evolution of a drop initially deformed by an external shear force. This method requires the following conditions: (1) the shape of deformed drop is axisymetrically ellipsoidal, (2) the drop and matrix polymer are stress and orientation free, and (3) the major axis should have a zero angle with the observation plane to reduce experimental errors. When a polymeric drop is sheared by polymeric matrix, the drop deforms into a flattened ellipsoid because of the normal stress,[23] and the major axis has non zero angle with the observation plane. It is also expected that the residual stress formed during deforming procedure does not disappear completely especially in the system that have long relaxation time. Therefore, the conditions aforementioned are not easy to attain by the conventional DDR method.

To solve these experimental difficulties, improved experimental techniques were proposed. Son and Yoon[24] and Mo et al.[25] demonstrated that at the late stage of the capillary instability process, the disintegrated droplets from a long thread follow the typical retraction process, which can be described by a well-known theoretical equation used in the conventional DDR method. The disintegrated droplets maintain axisymmetrical ellipsoidal shape, and the major axis of the drop has a zero angle with the observation plane without any residual stress. We call this method the retraction of disintegrated drops from the BT (DDR-BT).

Another improved technique was proposed by Son and Migler.[26] They showed that at the late stage of the typical IFT method, a short fiber transforms into the axisymmetrical ellipsoid. Then, the relaxation of the ellipsoid can be described by the theoretical equation used in the conventional DDR method. This method also overcomes the experimental difficulties encountered in the conventional DDR method. We call this method the retraction of ellipsoidal drop from the imbedded short fiber (DDR-IFR).

In this paper, we present experimental comparison of five methods, which include (i) BT, (ii) imbedded short fiber retraction, (iii) retraction of deformed (sheared) drop after cessation of flow, (iv) retraction of disintegrated ellipsoidal drops from the BT, and (v) retraction of ellipsoidal drop from the imbedded short fiber. Two improved DDR methods (DDR-BT and DDR-IFR) are compared in detail. All the methods were carried out at the same temperature for a model polymer pair: polystyrene (PS) and polyamide 6 (PA-6).

EXPERIMENTAL

Materials

Two polymers are used in this study. Polyamide-6 (PA-6) was purchased from Polysciences Inc. (M_n = 16,000). Polystyrene (PS) was obtained from Dow Chemicals (trade name: Styron 666D).

Rheological measurement

Zero-shear viscosity is critical to get an exact interfacial tension in the transient dynamic method. They were obtained by measuring the shear viscosity at various shear rates (10^{-2} to 5 s^{-1}) in the steady mode. The polymers used in this study show a Newtonian behavior at the shear rate of 10^{-2} to 10^{-1} s^{-1}. The rheometer used is an Advanced Rheometric Expansion System (ARES). A parallel plate configuration (diameter = 25 mm) was used with a gap of about 1.0 mm. The temperature for the measurement was 230°C. Measured zero-shear viscosities of PA-6 and PS were 300 and 1200 Pa s, respectively.

Measurement of interfacial tension

The interfacial tension between PA-6 and PS was measured by five methods as mentioned earlier. Pellets of PA-6 and PS were dried in a vacuum oven at 80°C overnight prior to molding and drawing. Disks of PS in 1-mm thickness and 25-mm diameter were pressed at 180°C between two metal plates on a Carver Laboratory Press. The PA-6 fibers were obtained by drawing from the molten pellets at 230°C. Diameter ranged from 50 to 300 μm. The fibers were cut to 20-mm length and were annealed at 80°C for about 24 h in a vacuum oven prior to cutting to a short fiber (ranging 0.5–3 mm in length) for the IFR and DDR method. During the drawing the fibers, special care was taken to prevent the absorption of moisture into the PA-6 fiber. The PA-6 fibers were stored in a vacuum oven at 50°C to avoid further absorption of moisture. We only used PA-6 threads that have been stored for less than 1 week, to avoid deterioration of the sample. An Optical Shearing System (model Linkam CSS 450) connected to a super VHS videocassette recorder and to a Zeiss transmission optical microscope was used. This device enables the sample to be simultaneously sheared and heated under microscopic observation.

We performed the five different interfacial tension measurements by employing the following protocol depicted in Figure 1. In all transient dynamic methods, the interfacial tension is obtained by observing the shape evolution of the polymer–polymer interface. So,

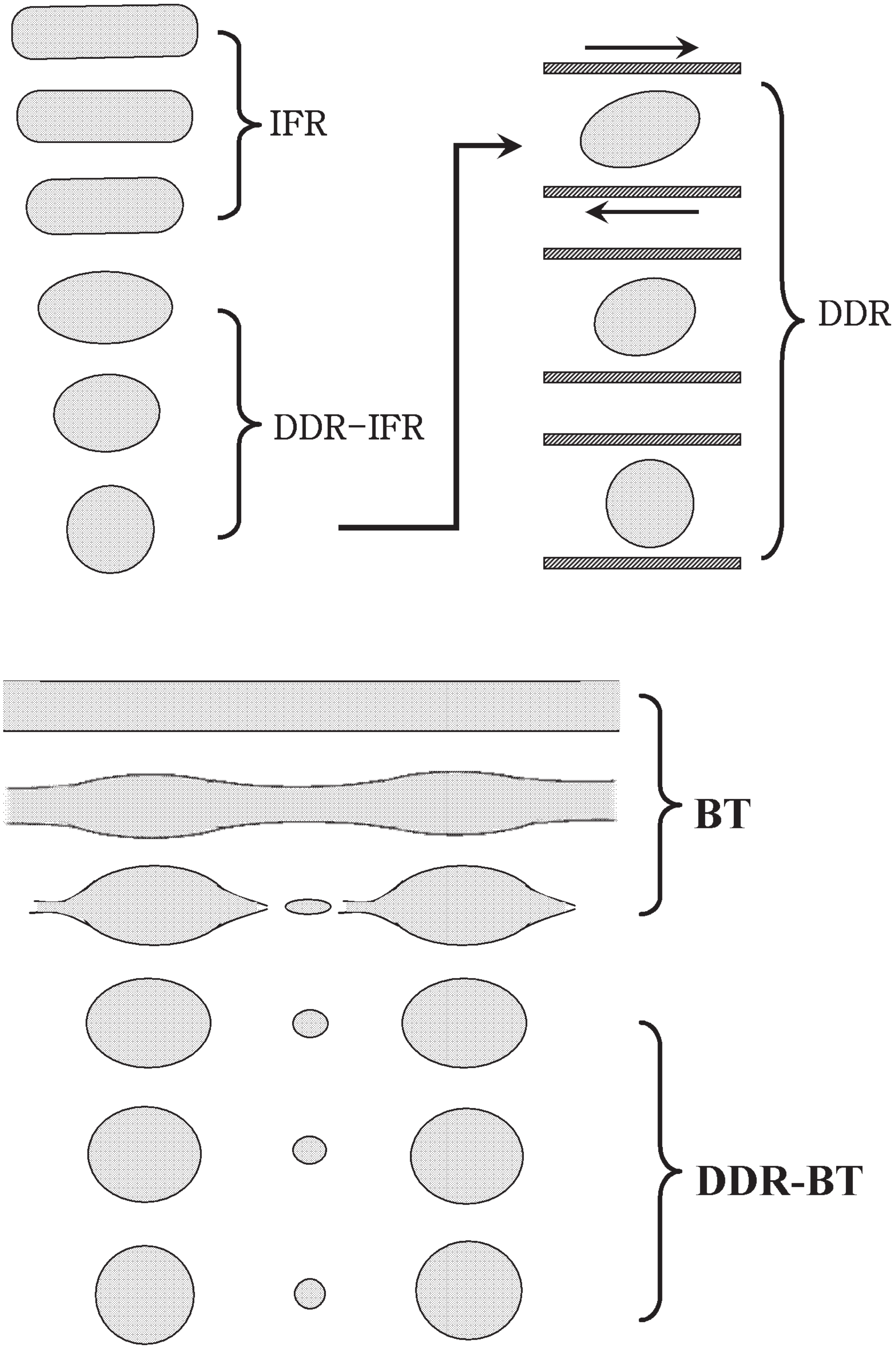

Figure 1 Schematic illustrations describing five techniques for the interfacial tension measurement demonstrated in this study.

the difference between the methods lies basically in the initial shape of the interface. In the BT method, a long thread of length at least 60 times longer than the diameter was placed between two films of PS. In the IFR method, a short fiber of length less than 10 times of the diameter was placed between two films of PS. This sandwiched sample was placed in the shearing device, under the microscope. At first, the temperature was increased and maintained at 200°C for 10 min to ensure perfect imbedding without any undesired de-

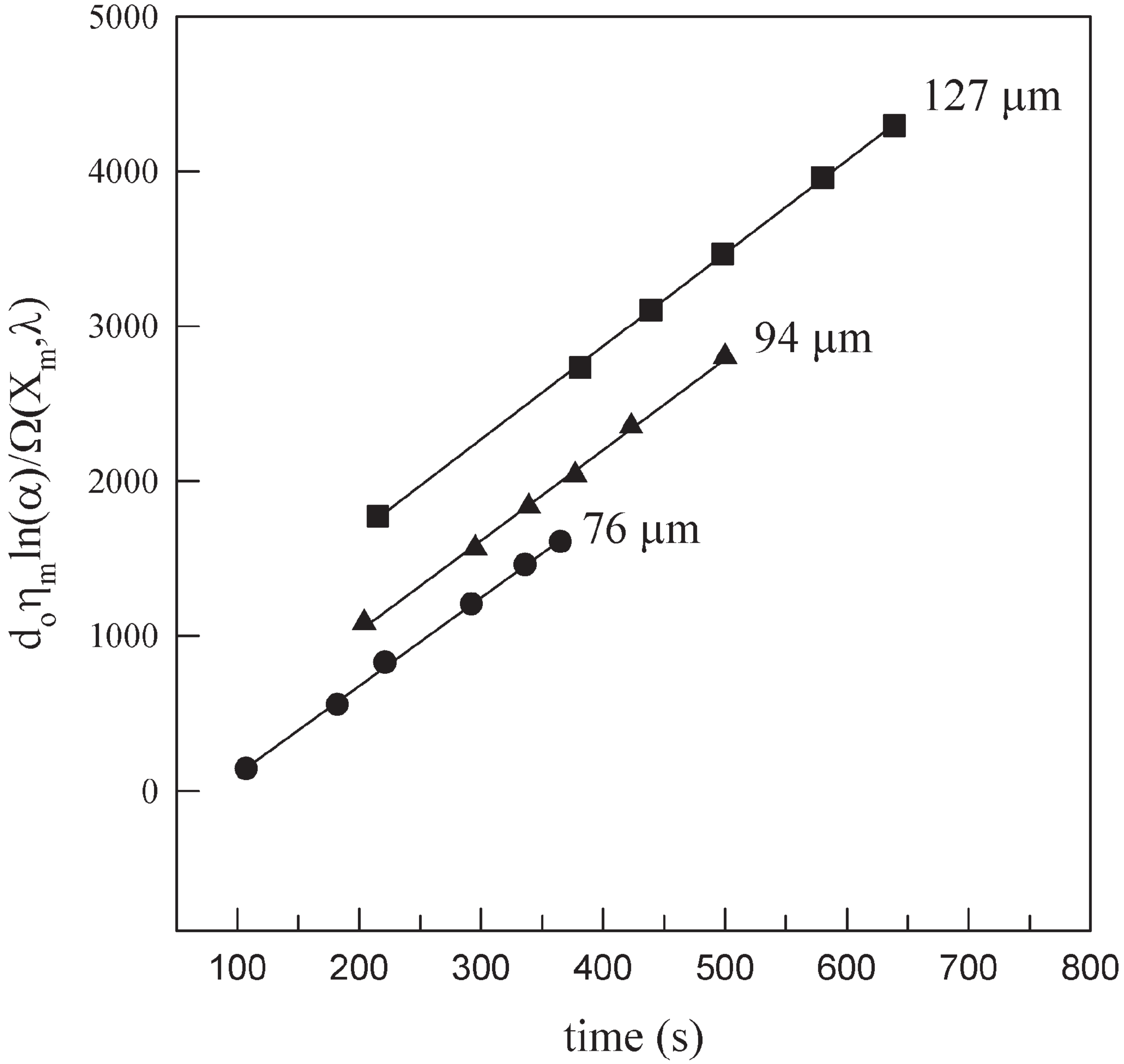

Figure 2 Plot of $\eta_m d_0 \ln(a)/\Omega$ versus time. The numbers indicated in the graph are the initial thread diameters.

formation of the PA-6 fiber (T_m = 216°C). The gap between the two glass walls was then adjusted very slowly to the desired size, ranging from 1.5 to 2.5 mm, depending on the diameter of the fiber. The temperature was then increased to 230°C. To obtain measurements, images from the microscope were recorded onto a videotape. In the case of the long-fiber imbedding, the initial process is described by the capillary instability mechanism. We used the Tomotika's equation to extract the interfacial tension (BT method). In the late stage of the capillary instability process, the thread disintegrates and transformed into isolated drops. The disintegrated drops follow a typical retraction process. We used Luciani et al.'s equation to extract the interfacial tension by observing this late stage (DDR-BT).

In the case of the short-fiber imbedding, the fiber is described as a retracting cylinder capped with two hemispheres, and we used Carriere et al.[14–16] method to extract the interfacial tension (IFR). In the late stage of retraction, it was observed that the short fiber transforms to a perfect axisymmetrical ellipsoid. Thus, the images captured at the late stage of the whole retraction process were used to calculate the interfacial tension by the DDR method (DDR-IFR). After an IFR was completed, the equilibrium spherical drop was deformed by applied shear force. Typical shear rates applied were 0.05 to 0.2 s^{-1} for about 10 s. The images

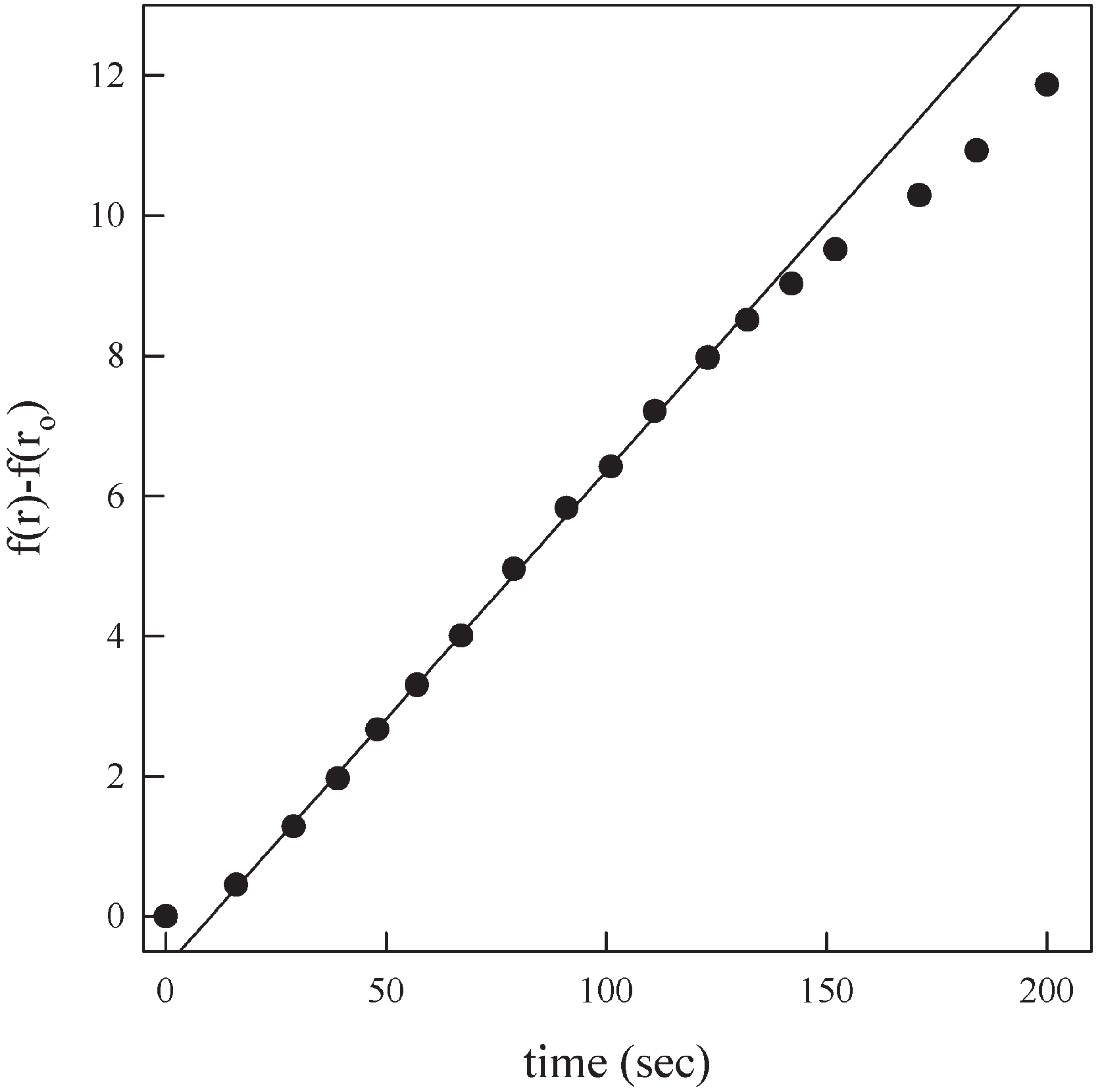

Figure 3 A typical plot of $f(r) - f(r_e)$ versus retraction time.

during the subsequent retraction process were then recorded. Thus, we also obtained and analyzed the data for interfacial tension via conventional DDR method.

RESULTS AND DISCUSSION

Breaking thread method

According to the theory describing the disintegration of a cylinder thread immerged in another fluid, developed by Tomotika,[20] the distortion grows exponentially with time:

$$\alpha = \alpha_0 \exp(qt) \tag{1}$$

where α_0 is the initial amplitude and the growth rate of this distortion, q, is given by:

$$q = \frac{\sigma\Omega(X_m, p)}{\eta_m d_0} \tag{2}$$

where σ is the interfacial tension, η_m is the viscosity of the matrix, p is viscosity ratio, and d_0 is the initial thread diameter. The function, $\Omega(X_m, p)$, can be obtained from Tomotika's original paper. With a typical set of optical micrographs for the distortion growth of a PA-6 thread in PS matrix at 230°C, we obtain the interfacial tension from the slope by plotting $\eta_m d_0 \ln(\alpha)/\Omega$ versus time. Figure 2 shows typical plot of

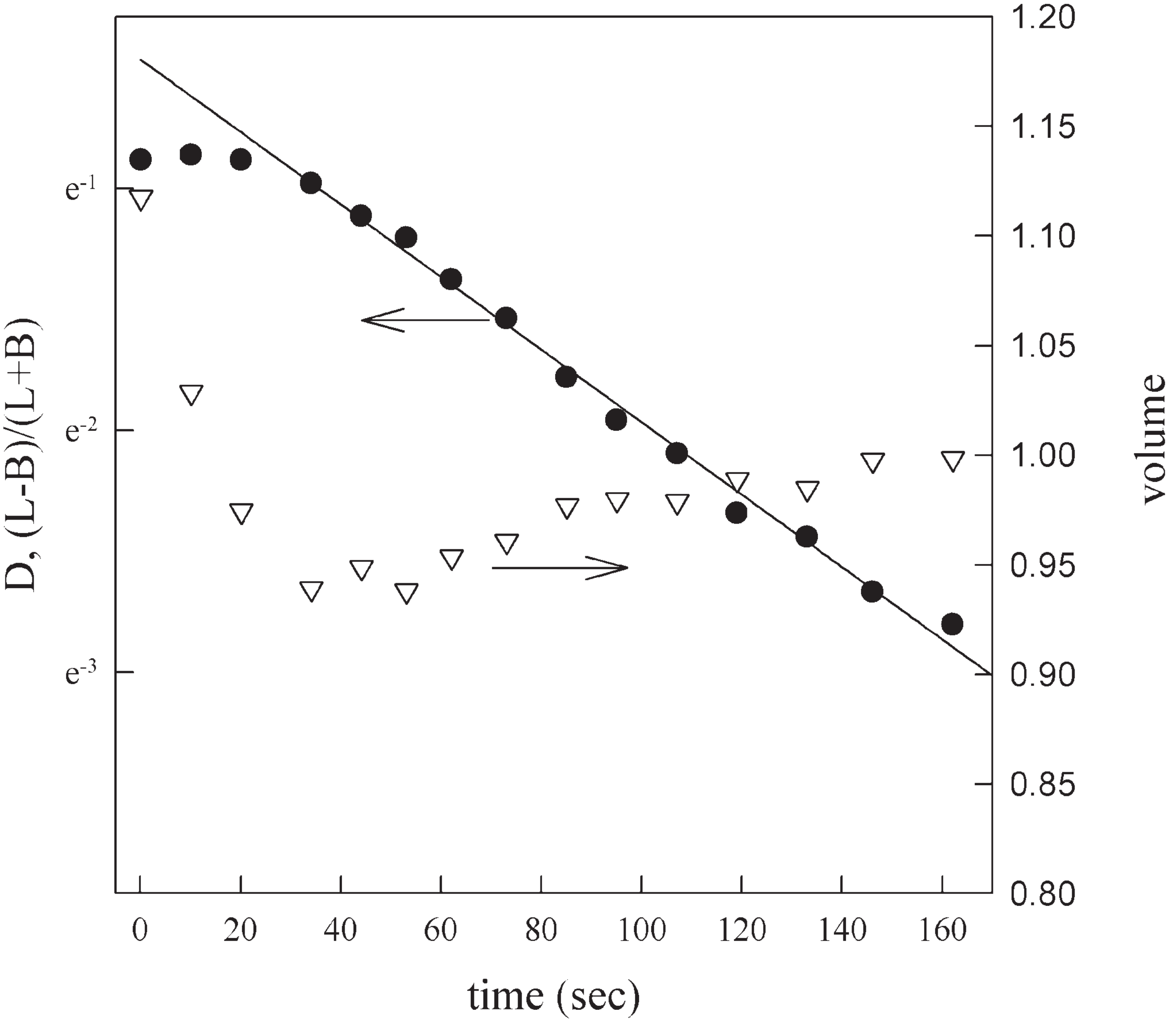

Figure 4 Time evolution of deformability factor D and the dimensionless apparent volume.

$\eta_m d_0 \ln(\alpha)/\Omega$ versus time. The slope of this plot is the interfacial tension. No significant variation in the interfacial tension with initial thread diameter is observed. The interfacial tension between PA-6 and PS obtained by the BT method is 5.7 ± 0.49 mN/m. This value is reasonable in compared with the values reported elsewhere.[12,14]

Imbedded short-fiber retraction

Carriere et al.[14–16] modeled a short fiber as a cylinder capped with two hemispheres, and expressed its shape evolution when it is imbedded in another polymer liquid as follows:

$$f\left(\frac{R}{R_0}\right) - f\left(\frac{R_e}{R_0}\right) = \frac{2.7}{(1.7\,p+1)}\frac{\sigma}{\eta_m R_0}t \qquad (3)$$

where R_0 and R_e are an equilibrium drop radius and an initial drop radius, respectively,

$$f(x) = \frac{3}{2}\ln\frac{\sqrt{1+x+x^2}}{1-x} + \frac{3^{1.5}}{2}\arctan\left(\sqrt{3}\,\frac{x}{2+x}\right) - \frac{x}{2} - \frac{4}{x^2} \qquad (4)$$

The other variables are the same as those shown in eq. (2). Figure 3 is a typical plot of $f(R/R_0) - f(R_e/R_0)$ versus retraction time. The interfacial tension is determined from the slope of the curve. We see that the initial period of the retraction is linear, but the data deviates from linearity at a later time when the shape of initially imbedded short fiber becomes ellipsoid.

We take this initial slope to calculate the interfacial tension. The interfacial tension value by the IFR method is 6.8 ± 0.30 mN/m.

Retraction of deformed (sheared) drop after cessation of flow

This method is based on the interfacial tension driven shape recovery of a slightly elongated drop. The basic equation is derived by Luciani et al.,[18] based on the Taylor theory[27] on the deformation of a pure viscous drop surrounded by a matrix fluid in steady shear flow. The equation takes the following form:

$$D = D_0 \exp\left\{ -\frac{40(p+1)}{(2p+3)(19p+16)} \frac{\sigma}{\eta_m R_0} t \right\} \qquad (5)$$

where D is the drop deformation parameter defined as $D = (L - B)/(L + B)$, L and B are, respectively, the major and minor axis of the ellipsoidal drop. D_0 is an initial deformation parameter. The other variables are same as those shown in eq. (3). The interfacial tension can be obtained from the slope by plotting $\ln(D)\eta_m R_0(2p + 3)(19p + 16)/(40p + 40)$ versus time. In Figure 4, the deformation factor and apparent dimensionless volume are plotted as a function of time. The apparent dimensionless volume is defined as $\pi LB^2/6$ (volume of axisymmetic ellipsoid, i.e., $B = W$) divided by the volume of the equilibrium sphere, $4\pi R_0^3/3$. Here, B and L for the calculation of the volume are directly measured from the photograph (which approximately corresponds to the real L multiplied by $\cos(\theta)$, where θ is an orientation angle), and L for the calculation of deformation is calculated by volume conservation, i.e., $L = 8R_0/B^2$. The apparent dimensionless volume at $t < 20$ s is greater than 1, indicating that the length of the observed minor axis is bigger than that of the other minor axis, *thus the drop is not axisymmetric*. The apparent volume decreases rapidly to a minimum and then gradually increases to a equilibrium value. During the retraction process, it is also observed that the tips of the elongated drop are out of focus under microscopic observation, representing that the major axis is not parallel to the observation plane. A plot of $\ln(D)$ versus time shows a linear relationship after this minimum of apparent volume. The interfacial tension value by the DDR method is 7.8 ± 0.82 mN/m.

Retraction of disintegrated drops from the bt

During the measurement of interfacial tension by the BT method, it is observed that the disintegrated drops from a long thread are of ellipsoidal shape, followed by a typical retraction process. In this procedure, it is believed that the drops are axisymmetrical ellipsoids because they are formed from an axisymmetrical cylinder under neither pressure nor external force. It is also expected that the major axis of the ellipsoid has zero angle with the observation plane, since the axis of the original thread is parallel to the observation plane.

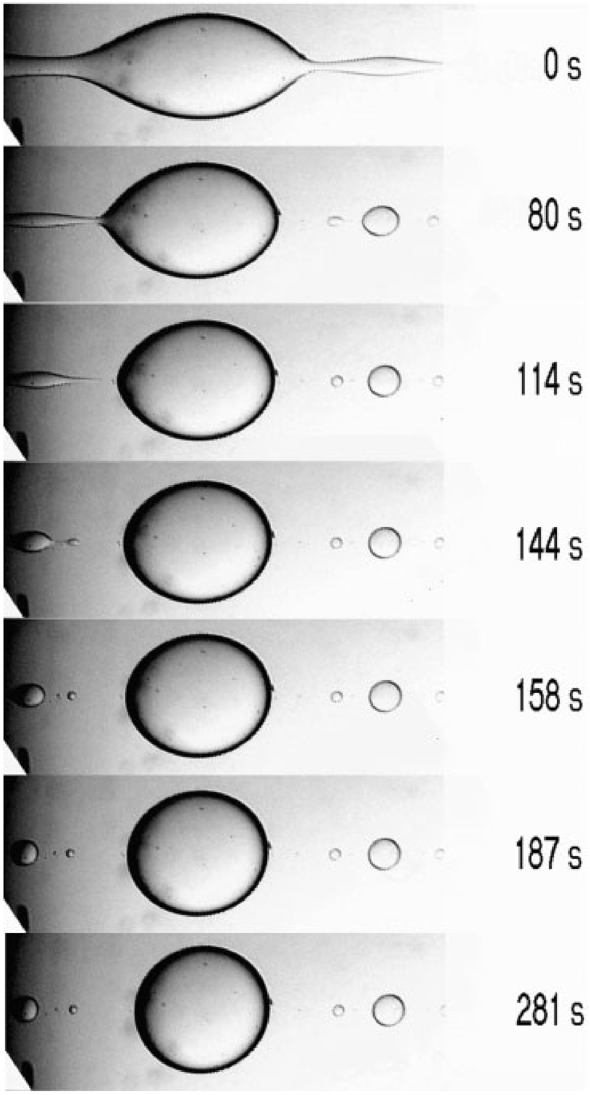

Figure 5 Optical micrograph of the retraction process for the PA-6 ellipsoidal drop disintegrated from a thread. Time (in sec) for the measurement is written beside each micrograph. The radius of spherical drop at equilibrium is 148 μm.

Figure 5 is a sequence of images for a typical retraction. Here, a PA-6 droplet is disintegrated from a long thread. The major axis of a drop is observed to be parallel to the observation plane, confirmed by the fact that both tips of the deformed drop are in clear focus of the microscope. This is also confirmed by a plot of the apparent dimensionless volume versus time shown in Figure 6. The calculated volumes are nearly unity regardless of elapsed time. If the major axis is not parallel to the observation plane, the calculated volume would increase gradually and approach an equilibrium value except for the very early stage. This

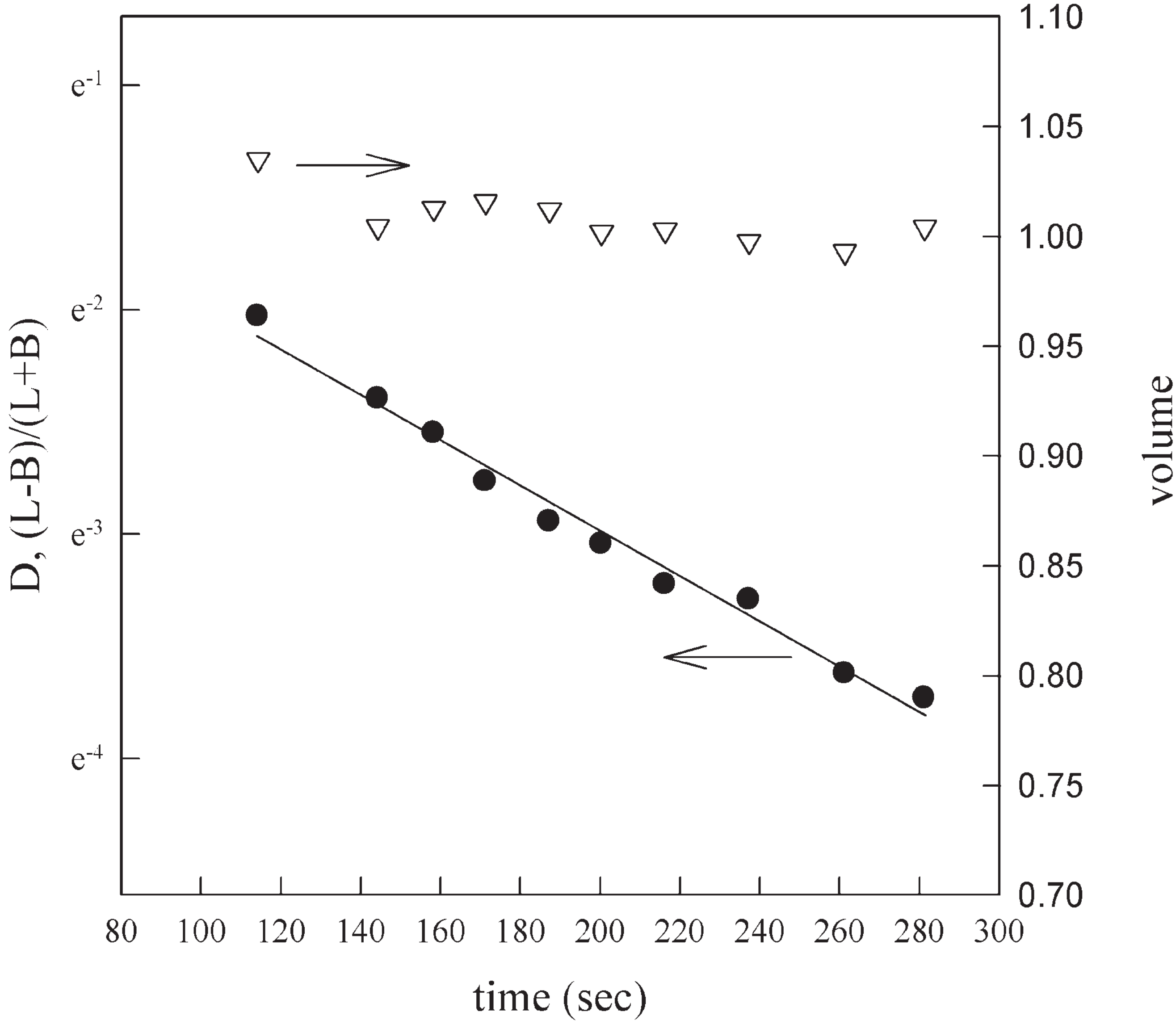

Figure 6 Time evolution of deformability factor *D* and the dimensionless apparent volume for the same experiment as in Figure 5.

plot also confirms that two minor axis (*B*, *W*) are same, which is the necessary condition to apply eq. (5) for the DDR method.

Interfacial tension measured by the DDR-BT is 2.7 ± 0.38 mN/m which is much lower than those by the other methods. Son et al. attributed this low interfacial tension value to the long elapse time before the test start. The polymer–polymer contact time during the measurements in the DDR-BT method is longer than those of the BT methods. As indicated by Luciani et al.,[18] due to the migration of the low molecular weight species and impurities toward the interface, the interfacial tension decreases with the time and approaches the equilibrium value. To confirm this, we repeat the conventional DDR experiment with the same drops already used for the BT and DDR-BT methods. This time, we shear the drops in the direction perpendicular to the initial long thread (the direction in which drops retract in DDR-BT process). The interfacial tension obtained by this protocol is 6.6 ± 0.44 mN/m, which is much higher than that by the DDR-BT. This implies that the long polymer–polymer contact time mentioned by Son and Yoon[24] is definitely not a cause for the low interfacial tension obtained by the DDR-BT. When we shear the drops in the same direction with the initial thread direction, the interfacial tension is much lower than that to perpendicular direction, though the value is somewhat higher than that by the DDR-BT. The fact that the drops retract very slowly in the direction parallel to the thread implies that the retraction is affected by the neighboring drops. In this study, the distance between drops is about 3 times of

TABLE I
Interfacial Tension Values Obtained by Various Methods Investigated in This Study

Method	Interfacial tension value (mN/m)
BT	5.7 ± 0.49
IFR	6.8 ± 0.30
DDR	7.8 ± 0.82
DDR-BT	2.7 ± 0.38
DDR-IFR	6.2 ± 0.43

the drop diameter. Because the matrix fluid at the mid-plane (mirror-plane) between drops cannot move in the direction perpendicular to the mid-plane and the distance between the drops is small, it is most likely that the mobility of the interface is hindered by this restriction. Thus, the DDR-BT method provides lower interfacial tension value unless the distance between drops are long enough (the case where the viscosity ratio of drop to matrix is extremely large or small), which is not general case in polymer blends. In this study, it is proved that the DDR-BT method is not proper to measure the interfacial tension.

Retraction of ellipsoidal drop from the imbedded short fiber

This method combines the analytical power of the DDR method with experimental simplicity of the IFR method. As shown schematically in Figure 1, during the measurement of interfacial tension by IFR method, the PA-6 short fiber transforms into an ellipsoid at the late stage. Then the relaxation of the ellipsoid is analyzed to extract the interfacial tension by the eq. (5). Because of the same reason and analysis as shown in Retraction of Disintegrated Drops from the BT section, it is confirmed that the major axis of the ellipsoid has zero angle with the observation plane and the shape of the PA-6 phase becomes a perfect axisymmetric ellipsoid after about 90 s. The interfacial tension obtained by this method is 6.2 ± 0.43 mN/m, which is consistent with the other methods except the DDR-BT. One more advantage of this method over the DDR-BT is that the initial D value is much higher, which reduces the experimental errors. In this study, the maximum D value in the DDR-IFR is e^{-2} to e^{-1}, whereas the D in the DDR-BT is e^{-3} to e^{-2}.

Table I shows the comparison of interfacial tension values obtained by the methods demonstrated in this study. All methods except the DDR-BT exhibit reasonably similar values. The interfacial tension value measured by the conventional DDR method is significantly higher than those measured by the other methods, though the variation is in an acceptable range. This could arise from a error in determining L and/or the residual stress caused by external shear stress. In all transient dynamic methods, the driving force to the equilibrium shape is assumed to be purely interfacial. Therefore, residual stress may cause the droplet to relax faster, yielding an interfacial tension value that is too large.[28]

CONCLUSIONS

We investigate five experimental techniques for the interfacial tension measurements. All methods except the DDR-BT exhibit reasonably similar interfacial tension values. The interfacial tension value obtained by the DDR-BT method is found to be much lower than those by the other methods. This is due to the effect of neighboring drops. The DDR-BT method is not appropriate for the interfacial tension measurement unless the distance between the neighboring drops are very long enough. Among all techniques, the modified DDR-IFR is found to be most convenient and accurate method.

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